NANOPOROUS CARBIDE DERIVED CARBON WITH TUNABLE PORE SIZE

This patent application claims the benefit of U.S. Provisional Patent Application Serial No. 60/484,840, filed July 3, 2003, which is herein incorporated by reference in its entirety.

Background of the Invention

Porous solids are of great technological importance due to their ability to interact with gases and liquids not only at the surface, but throughout their bulk. While large pores can be produced and well controlled in a variety of materials, nanopores in the range of 2 nm and below (micropores, according to IUPAC classification) are usually achieved only in carbons or zeolites. During the past decades major efforts in the field of porous materials have been directed toward control of the size, shape and uniformity of the pores.

Highly crystallized zeolites have a narrow pore size distribution, but discrete pore sizes and the fine-tuning of pore size is impossible in zeolites because pores are controlled by a lattice structure. Porous carbons produced by thermal decomposition of organic materials may have pore diameters down to 0.3 nm, or mesopores of several nanometers, but they typically have a broad pore size distribution that limits their ability to separate molecules of different sizes. Materials with a tunable pore structure at the atomic level and a narrow pore size distribution do not exist.

Selective etching of carbides is an attractive technique for the synthesis of various carbon structures from nanotubes to diamonds (Derycke et al. 2002 *Nano Lett.* 2:1043-1046; Gogotsi et al. 2001 *Nature* 411:283-287). Carbon produced by the extraction of metals from carbides

- 2 -

is called carbide-derived carbon (CDC)(Gogotsi, et al. 1994 *Nature* 367: 628-630; Gogotsi, et al. 1997 *J. Mater. Chem.* 7:1841-1848). Since the rigid metal carbide lattice is used as a template and the metal is extracted layer-by-

5 layer, atomic level control can be achieved during synthesis and the carbon structure can be templated by the carbide structure. Further structure modification and control can be achieved by varying the temperature, gas composition, and other process variables. Reaction (1):

10         $$SiC + 2Cl_2(g) = SiCl_4(g) + C$$
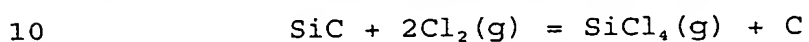
has been used for the production of silicon tetrachloride since 1918, but the remaining carbon was usually burned. The linear reaction kinetics of reaction (1) allows transformations to large depth, until the particle or

15 component is completely converted to carbon (Ersoy et al. (2001) *Mater. Res. Innovations* 5:55-62). The transformation is conformal and does not lead to changes in sample size or shape.

During the last decades, various CDCs have been

20 investigated and specific surface areas (SSA) of up to 2000 m^2/g with small pore sizes have been reported(Gogotsi et al. 1997 *J. Mater. Chem.* 7:1841-1848; Boehm et al. *Proc. 12th Biennial Conf. on Carbon* 149-150 (Pergamon, Oxford, 1975); Gordeevet al. 2000 *Phys. Solid State* 42: 2314-2317; Fedorov

25 et al. 1995 *Russ. Chem. J.* 39:73-83). Comparison of reported data on CDCs shows that, for different carbides (SiC, TiC, ZrC, B_4C, TaC, and Mo_2C) and chlorination temperatures, pores between 0.8 and 2.1 nm, determined by the structure of the carbide precursor and process

30 parameters, were produced. However, no control over the pore size or distribution was disclosed.

The present invention provides a method of tuning pore size in CDCs by controlling the synthesis temperature.

- 3 -

Summary of the Invention

An object of the present invention is to provide a method of producing a nanoporous carbide-derived carbon composition with a tunable pore structure and a narrow pore
5   size. The method of the present invention comprises extracting metals from a carbide using a halogen at elevated temperature to produce a nanoporous carbide-derived carbon composition with a tunable pore structure and a narrow pore size. Pore size is controlled by
10   selection of the carbide and/or the halogen. Tuning of the pore size is achieved by changing the extraction temperature.

Another object of the present invention is to provide nanoporous carbide-derived carbon compositions produced
15   with or without mesopores. Uses for these compositions include, but are not limited to, molecular sieves, gas storage, catalysts, adsorbents, battery electrodes, supercapacitors, water or air filters, and medical devices.

Brief Description of the Drawings
20   Figures 1a and 1b are graphs demonstrating the differential pore size distributions for CDCs produced in accordance with the method of the present invention. As shown, the pore sizes increase with increasing chlorination temperatures.
25   Figure 2a, 2b and 2c show data for seven CDC samples produced in accordance with the method of the present invention spanning elevated chlorination temperatures of between 300°C and 1400°C, demonstrating that pore size can be controlled with better than 0.05 nm accuracy.
30   Figures 3a and 3b show data from Raman spectroscopy indicating that carbon is formed at 200°C from initial carbide precursors.

- 4 -

Detailed Description of the Invention

The present invention provides a method of producing
a nanoporous carbide-derived carbon (CDC) composition with
a tunable pore structure and a narrow pore size. In the
5 method of the present invention, a metal carbide is exposed
to a halogen so that the metal is extracted from the
carbide. The inventors have found that this halogen
extraction, when performed under elevated temperatures,
produces a nanoporous carbide-derived carbon composition
10 with a tunable pore structure and a narrow ranges of pore
sizes. Desired pore sizes can be achieved through
selection of the halogen and/or the carbide.

Halogens useful in the present invention include
fluorine, chlorine, bromine, and iodine. The halogen may
15 be in the form of a gas or liquid. By halogen gas it is
meant to be inclusive of any gas or gas mixture which
comprises at least one halogen. Further, the halogen gas
may contain multiple halogens. In a preferred embodiment,
the halogen is in the form of a chlorine containing gas or
20 a gas mixture containing chlorine and argon (Ar).

The pore size can be selected by changing the
halogen. The heavier the halogen used, the larger the
resulting pores. Likewise, the smallest pores are produced
by fluorine, with larger halogens like chlorine, bromine
25 and iodine producing larger pores.

The carbide used in the present invention may be any
suitable carbide. Examples of suitable carbides include,
but are not limited to, SiC, TiC, ZrC, B_4C, TaC, and Mo_2C.
By utilizing different carbides, the pore sizes can also be
30 tuned to a selected or desired size. Thus, both the
halogen and the carbide may be chosen to provide a desired
pore size.   In a preferred embodiment the carbide is
Ti_3SiC_2. CDC produced from Ti_3SiC_2 has a more narrow pore
size distribution than single wall carbon nano-tubes or
35 activated carbons, and it has a pore size distribution that

is comparable to that of zeolites. Ti_3SiC_2 is available in different forms including powders and bulk samples. Ti_3SiC_2 is a soft ceramic with a lamellar structure which can easily be machined to any shape. Etching of Ti_3SiC_2
5 generates a larger pore volume, about 75%, as compared to TiC or SiC which are about 56.2% and 57.3%, respectively.

      The method of the present invention allows tuning the porosity of carbide-derived carbons (CDCs) with sub-Ångström accuracy in a wide range by controlling the
10 halogen temperature. The desired pore size of the composition is achieved by selection of a halogen and of a carbide each for their respective tuning ability. Elevated temperatures for the halogen extraction are then chosen to selectively tune the carbide composition. Preferably the
15 CDCs of the present invention are produced at elevated temperatures from between 200°C to 1400°C. CDCs can be produced as a powder, a coating, a membrane or parts with near final shapes. The CDC may be produced with or without mesopores. When the elevated temperature is above 700°C,
20 isotherms of CDCs are produced with the presence of mesopores.

      Tunable pore size can be achieved with the method of the present invention with at least 0.05 nm accuracy.

      For example, the inventors have found that
25 chlorination in a flow of pure Cl_2 for 3 hours in a quartz tube furnace results in extraction of Ti and Si from Ti_3SiC_2 leading to the formation of carbon by the reaction:

$$Ti_3SiC_2 + 8Cl_2(g) = SiCl_4(g) + 3TiCl_4(g) + 2C.$$
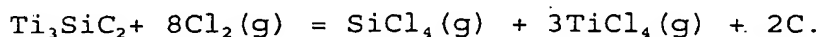
      Several different techniques were independently used
30 to measure the resulting pore size. These included argon (Ar), and methyl chloride (CH_3Cl) sorption, as well as small-angle X-ray scattering (SAXS). As shown in Figures 1a and 1b, the pore sizes of CDCs increase with increasing temperature. The differential pore size distributions for

- 6 -

CDC as measured by methyl chloride are illustrated in Figure 1a. The differential pore size distributions for CDC as measured by argon adsorption technique are illustrated in Figure 1b. No mesopores or macropores were

5 detected at 300-500°C. A small volume of mesopores of 2-4 nm in size appeared at 700°C, and the volume of mesopores increased sharply at 1100°C and above. Pore size distributions were calculated using the Horvath-Kawazoe method and assuming a slit pore model. Ar adsorption was

10 measured at -186°C. The sorption isotherms of low-temperature CDCs (up to 600 °C) obtained using N_2, Ar, or, CH_3Cl were of type I in the Brunauer classification, which is evidence of the presence of nanopores and the absence of meso- or macropores. This is in agreement with the

15 differential pore size distributions shown in Figure 1a. Very small pore sizes were achieved at low temperatures; just slightly larger than the interplanar spacing in graphite (0.3354 nm). Remarkably, the pore size distributions are very narrow (Figure 1a) and close to

20 those of VPI-5 zeolite.

Isotherms of CDCs produced above 700°C were of type IV, which indicates the presence of mesopores. Total pore volumes observed for the samples produced at 700°C, 900°C, and 1100°C were almost the same, but the pore size

25 distributions were different.

Mesopore volume and size was found to increase with increasing chlorination temperatures. Their equivalent radius was less than 3 nm at 700°C (Figure 1a) and about 6 nm at 1100°C (Figure 1b). Weight loss and energy-dispersive

30 X-ray spectroscopy (EDS) analysis of the samples after chlorination suggested almost complete removal of Ti and Si above 400°C.

Since the CDCs retained the original volume of the carbide precursor, it is fair to assume the total pore

35 volume to be the same after chlorination at different

temperatures. The maximum pore volume of about 0.64 cm^3/g
accessible to Ar and N$_2$ in CDC after heat treatment at 700°C
to 1400°C is in agreement with the theoretically calculated
value of 0.645 cm^3/g. SAXS measurements confirm the
5 evolution of pore size with increasing processing
temperature.

        Figure 2 shows data for 7 samples spanning the range
between 300°C and 1200°C and demonstrating the dependencies
of gyration radius(R$_g$)and pore size on chlorination
10 temperature. Figure 2a shows experimental SAXS curves in
Guinier coordinates; Figure 2b shows a distribution of
gyration radius m(R$_g$); and Figure 2c shows a comparison of
pore sizes obtained by CH$_3$Cl sorption and SAXS for different
chlorination temperatures of Ti$_3$SiC$_2$. No pores with R$_g$ larger
15 than 0.6 nm were detected by SAXS. The SAXS-derived R$_g$ at
600°C is 0.53 nm, while the sorption-based D$_m$ (average of
500°C and 700°C values) is 0.61 nm. Taking the latter as the
height of slit pores, the implied R is 0.71 nm, comparable
to the radii of slit-shaped nanopores in polymer-derived
20 materials. Thus, slit pores have been formed in CDC.
Extremely fine tuning of pore sizes is possible between
300°C and 800°C. At higher temperatures, growth of mesopores
volume occurs at the expense of nanopores. The results
have been corrected for background and scattering by the
25 quartz container. Monodisperse Guinier behavior is
observed, log(I) approximately -Q^2 (R$_g$)^2 /3 over a broad
range of Q^2 (Figure 2a), as evidenced by the fact that the
analysis gives a very narrow peak in m(R$_g$) which accounts
for most of the nanopore volume (Figure 2b).
30   The analysis of the CH$_3$Cl sorption data assumed slit
pores, which implies that the sizes in Figure 1 are
associated with the height of the slits. Slit pores are the
logical choice, given the layered nature of the precursor
material. For slit pores approximated as cylinders of
35 radius R and height D, $R_g^2 = D^2/12 + R^2/2$. SAXS confirms the

aforementioned sorption data and shows that pore size can
be controlled with better than 0.05 nm accuracy (Figure
2c). This result is remarkable in that it has never been
demonstrated for any other porous material.

5   Microstructural studies of CDCs were conducted to
explain their structural reorganization and the development
of their porous structure with temperature. With
increasing temperature, the specific distance for jump of
carbon atoms increased and the pore size increased

10 accordingly.

          Raman spectroscopy shown in Figures 3a and 3b
demonstrate that carbon already forms at 200°C. However,
XRD shows peaks of the initial carbide; thus the
transformation was not complete at this temperature. Raman

15 spectra and TEM micrographs of CDC were produced at
different temperatures. Figure 3a illustrates the Raman
spectra of CDC synthesized at different temperatures. A low
position of G-band and upshifted D-band in the Raman
spectrum is likely the result of carbon bonding to Si and

20 significant sp^3 hybridization of carbon. Si (<15%) was
detected by EDS in the samples chlorinated at 300°C,
showing that Ti was preferentially etched at lower
temperatures. Different rates of Si and Ti reaction were
also observed in carburization and silicidation of Ti_3SiC_2

25 above 1400°C (El-Raghy et al. 1998 *J. Appl. Phys.* 83:112-
119). Figure 3b demonstrates the temperature dependence of
I_D/I_G ratio and provides TEM images showing evolution of the
carbon structure with temperature. CDC produced in
temperature range I (300°C) is completely amorphous. Slow

30 pore growth occurs in range II. Formation of carbon fringes
at 700°C and higher temperatures show the beginning of the
structure ordering leading to increasing pore size and
appearance of mesopores in range III. Pronounced
graphitization is observed at 1200°C (range IV), resulting

35 in a sharper G-band in the Raman spectrum and decreased

I_d/I_g ratio.

Ti can be extracted by Cl_2 at lower temperatures than
Si. Complete removal of Si from CDC and a decreased amount
of trapped chlorine leads to an increase in pore volume
5   from 0.25 cm^3/g at 300°C to 0.645 cm^3/g at 700°C. A slow
increase in intensity and downshift of the D-band in the
Raman spectra are observed with increasing temperature.
According to high-resolution TEM analysis and selected area
diffraction, the CDC samples produced at lower temperatures
10   were completely amorphous. Noticeable ordering of graphite
starts at 700°C and nanocrystalline graphite appears at
1200°C. The FWHM of the G-band decreases slightly above
600°C, but only at 1200°C does Raman spectroscopy show the
formation of ordered graphitic carbon.
15   Total volume and characteristic dimensions of meso-
and nanopores can be controlled by selection of a binary or
ternary carbide or a carbide solid solution and variation
of the chlorination process parameters. For example, carbon
derived from SiC at 900°C has a narrow pore size
20   distribution and an average pore size of 0.65 nm, similar
to CDCs produced from Ti_3SiC_2 at 700°C, but with no
mesopores. Carbon made from SiC at 1200°C had a pore size
of 1.2 nm, and SiC and B_4C derived carbons have values from
0.8 to 2.1 nm. Depending on the carbide structure, the pore
25   volume of CDCs can vary from ~50% to ~80%. CDCs derived
from Ti_3SiC_2 have the theoretical density of 0.55 g/cm^3. CDC
samples are hydrophilic and adsorb water quickly; rapidly
sinking in water. However, if the surface is sealed with a
sealing compound, lacquer, polymer, nail polish or other
30   suitable sealant, they float because their density is well
below 1 g/cm^3.

It is notable that CDCs do not have macroporosity if
produced from a dense ceramic or a carbide single crystal.
However, a controlled amount of macroporosity can be
35   introduced by using sintered porous ceramics.

- 10 -

Macroporosity or mesoporosity, that appears at high
chlorination temperatures, is not desirable for
molecular sieve membranes, but would be necessary for
catalytic and some other applications, because it allows
5   easier access to nanopores. Based on their tunable porous
structures, controlled surface chemistry, and other
properties, CDCs may be used for some applications where
single-wall carbon nanotubes are currently considered. For
example, CDC is an attractive material for electrodes for
10 electrochemical double-layer capacitors commonly called
"supercapacitors" because the pore size distribution can be
tuned to match various electrolytes.

Hydrogen uptake depends on the porous structure of
the adsorbent. The highest uptake was achieved in
15 nanoporous carbons with SSA above 1000 m^2/g and almost no
mesopores. CDCs produced at 600°C and 1100°C have SSA of
1061 m^2/g and 1431 m^2/g, respectively, and SSA of up to 2000
m^2/g has been measured for SiC- and B_4C-derived CDC. The
ability to tune the pore size to exactly fit the hydrogen
20 (or other gas) molecule is of principal importance for gas
storage applications. About 40 wt.% Cl_2 is trapped in CDCs
produced at 300-400°C at room temperature and ambient
pressure, if the cooling is done in argon, and it can reach
55-60 wt.% when cooled in Cl_2. The amount of Cl_2 stored
25 decreases with increasing pore size, reaching less than 5
wt.% at 1200°C. The stored chlorine is slowly released,
and its amount goes down to approximately 20 wt.% after
storage for ten days in open air.

Fast release of atomic chlorine is observed upon
30 heating in He up to 600°C at 10°C/minute. Attempts to
measure SSA of CDC produced at 300°C by the BET method
resulted in the unreasonably low values of 162 m^2/g for N_2
and 382 m^2/g for Ar. This clearly shows the selectivity of
CDC to different gases. A significant volume of nanopores
35 inaccessible to large molecules may allow for the

- 11 -

separation of hydrogen from N_2 and other gases. Further, the combination of near-net shape and very mild chlorination temperatures are not only unique to Ti_3SiC_2, but also bode well for the inexpensive mass production of CDC components,

5   which, unlike zeolites, can have a large size and complex shape.

The following nonlimiting examples are provided to further illustrate the present invention.

EXAMPLES

10   Example 1: Calculation of Total Pore Volume

Total pore volume $(V\Sigma)$ and average pore size were calculated from Ar and CH_3Cl adsorption isotherms according to HK (Horvath and Kawazoe) theory. Specific surface area, according to BET (Brunauer, Emmet, and Teller) theory

15   and nanopore volume, was calculated using t-plots based on the CH_3Cl or Ar sorption isotherms. Nitrogen adsorption did not produce reliable results on samples with a pore size smaller than 1 nm. Ar adsorption (Micromeretics ASAP Pore Analyzer) was used to measure pore sizes above and under 1

20   nm, but the technique required long periods of time (5 days) for equilibration and could not produce the full distribution when the pore size approached 0.5 nm. The methyl chloride adsorption isotherms were used to measure the pore size below 0.7 nm assuming a slit pore shape.

25   Example 2: Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) was performed on a multi-angle diffractometer equipped with a Cu rotating anode, double-focusing optics, evacuated flight path and 2-D wire detector. Data was collected over the Q range 0.005-

30   1.4 $Å^{-1}$. Powder samples were loaded into 1.5-mm-diameter quartz capillary tubes and measured in transmission for 1 hour. The scattering intensity from an empty capillary was then collected and subtracted with sample absorption. corrected. Expecting a finite but narrow

- 12 -

distribution of radii of gyration R_g, a modified Guinier
analysis was employed to obtain the mean pore size and
distribution. The fraction volume of pores of a given size
was then estimated for each sample. By deconvoluting the
5 experimental $\ln(I)$ vs. Q^2 curves into components
corresponding to pores with different R_g, distribution
functions of R_g were found.

Example 3: Determination of Structure of CDCs

    Raman microspectroscopy (Renishaw 1000, Ar ion laser,
10 514.5 nm), transmission electron microscopy (TEM, JEOL
2010F), energy-dispersive spectroscopy (EDS) and X-ray
diffraction (XRD, Siemens), were used to study the
structure of CDC powders. In-plane crystal size of
graphite L_a was calculated by the Tuinstra and Koenig
15 equation: $1/L_a = I_D/I_g$, where I_D and I_g are intensities of
disorder-induced D band and graphite G band, assigned to
zone center phonons of E_{2g} symmetry.